



Research articles

Magnetic phase separation and unusual scenario of its temperature evolution in porous carbon-based nanomaterials doped with Au and Co



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ABSTRACT

Two porous glassy carbon-based samples doped with Au and Co were investigated. The magnetization study as well as measurements of the nonlinear longitudinal response to a weak *ac* field (NLR) and electron magnetic resonance give evidences for a presence of magnetic nanoparticles (MNPs) embedded in paramagnetic/ferromagnetic matrix respectively, both samples being in magnetically phase-separated state at temperatures above 300 K. Matrix, forming by paramagnetic centers located in matrix outside the MNPs, reveals exchange interactions providing its ferromagnetic (FM) ordering below $T_C \approx 210$ K in Au-doped sample and well above 350 K in Co-doped one. For the former, NLR data suggest a percolation character of the matrix long-range FM order, which is mainly caused by a porous amorphous sample structure. Temperature dependence of the magnetization in the Au-doped sample evidences presence of antiferromagnetic (AF) interactions of MNPs with surrounding matrix centers. At magnetic ordering below T_C these interactions promote origination of “domains” involving matrix fragment and surrounding MNPs with near opposite orientation of their moments that decreases the magnetostatic energy. On further cooling, the domains exhibit AF ordering below $T_{tr} \sim 140$ K $< T_C$, resulting in formation of a peculiar “ferrimagnet”. The porous amorphous structure leads to absence of translational and other symmetry features through the samples that allows canted ordering of magnetic moments in domains and in whole sample providing “canted ferrimagnetism”. At low temperatures $T_{tr} \sim 3$ K, “order-order” transition, evidencing the non-Heisenberg character of this magnetic material, occurs from ordering like “canted ferrimagnet” to FM alignment, which is stimulated by external magnetic field. The data for Co-doped sample imply the similar evolution of magnetic state but at higher temperatures above 350 K. This state exhibits more homogeneous arrangement of the FM nanoparticles and the FM matrix. Order-order transition occurs in it at higher $T_{tr} \sim 10$ –15 K as well and followed by formation of long-range FM ordering found earlier by neutron diffraction. Doping of carbon-based nanomaterials by magnetic metals provides advantages for their possible practical applications as Co-doped sample with higher T_C (>350 K) and larger remanent magnetization evidences.

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1. Introduction

Nowadays, it is evident that carbon-based nanomaterials represent a novel class of ferromagnetic (FM) matter, which does not contain basically any FM metal components [1]. Such materials attract considerable attention due to a high-temperature FM

behavior (with the Curie temperature T_C above room temperature) observed in various carbon structures, accompanied with the magnetic hysteresis and the remanent magnetization [1–3]. The listed features make these materials quite attractive for applications both in technique (spintronics, light magnets) and in biology as well as in medicine, the latter being connected with low toxicity due to vanishing concentration of metallic elements [1,2].

Well known bulk carbon materials, such as graphite and diamond with ignorable content of defects and impurities, reveal diamagnetic behavior [1,2,4]. While induction of defects, for

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example by proton irradiation of graphite, is accompanied by appearance of some FM characteristics [2,5–7]. It is widely believed that namely generation of defects or disorder in a host matrix leads to unconventional magnetic properties of carbon-based materials [1,2,8].

Experimental investigations establishing intrinsic magnetism of defect-rich carbon structures [1,2,7] have been supported by extensive theoretical work. Namely, the FM behavior has been predicted in such structures as (i) graphite surface with negative Gaussian curvature [9]; (ii) a mixture of carbon atoms with alternation of the $sp^2 - sp^3$ bonds [10]; (iii) those containing the graphene zigzag edges [11,12]; (iv) disordered graphite with random monatomic defects [13]. In turn, theoretical values of a local magnetic moments $\mu \sim 1\text{--}2 \mu_B$ connected with intrinsic defects or disorder [14,15], have been supported by experimental investigations of highly-oriented pyrolytic graphite yielding $\mu \sim 0.2\text{--}1.5 \mu_B$ per defect at the distance between defects $\sim 0.5\text{--}4 \text{ nm}$ [16]. A possible role of magnetic impurities in origination of FM ordering of carbon-based materials is under question till now [1,2].

To clarify this question it seems interesting comparative investigations of glassy carbon-based nanomaterials doped by non-magnetic (for example Ag, Au etc.) and magnetic (for example Co, Ni, Fe etc.) metal ions. Both variants of doping introduce structure perturbations, which can induce appearance of magnetic moments, while only the latter variant moreover introduced the moment directly, and comparison of magnetic properties of such materials can elucidate the problem. Corresponding investigations were performed in recent works [17,18], where non-doped powder nanocarbon sample and porous glassy carbon samples doped with Ag, Au and Co were investigated. The most complete information was obtained on compounds doped with Au and Co [18]. According to the nuclear magnetic resonance data, the local structure of these samples was composed of the aromatic and aliphatic organic fragments. Their random distribution, typical of the amorphous structure, was found from the neutron diffraction investigations. Magnetic properties of these compounds were attributed to a presence of multiple intrinsic defects acting as PM centers, which were stabilized in aromatics providing their interactions [18]. However, details of the evolution of magnetic state of these composites with complex porous structure are completely unclear. Usually their magnetism is explained by a presence of magnetic nanoparticles (MNP) with short-range FM ordering and their magnetic alignment. The long-range FM ordering found from neutron diffraction at low temperatures together with a presence of such MNPs following from magnetization data allow one to suggest several scenarios of final long-range magnetic ordering: (i) percolation type long-range FM ordering of magnetic nanoparticles (MNPs) only; (ii) formation of phase-separated (PS) magnetic state consisting of MNPs embedded in PM matrix in critical regime followed by long-range FM ordering as well. In the latter case there are a few possible ways to FM final state again: (i) matrix FM ordering without involving MNPs very weakly interacting with matrix; (ii) formation of their common FM alignment. To our knowledge there are no systematic investigations of this issue in carbon-based materials.

One more important problem of glassy porous carbon-based compounds is the irreproducibility of sample magnetic properties at a new synthesis [1–3]. It can be assumed that a plausible reason for this is spatial inhomogeneity of synthesized samples accompanied by magnetic heterogeneity that seems likely for amorphous porous structure found from neutron diffraction [18].

We present here systematic investigation of magnetic properties of porous glassy carbon-based nanomaterials doped by Au and Co including measurements of longitudinal nonlinear response to a weak ac field (NLR), electron magnetic resonance (EMR) as

well as magnetization. The first of them was very informative in investigation of PS in complex systems with strong electron correlations, manganites and cobaltites [19–21 and references therein], since permits one to select contributions of matrix and cluster subsystem due to their different nonlinear properties. Both studied samples exhibit magnetic phase separation which starts from high temperatures and is characterized by a presence of MNPs embedded in para(ferro)magnetic matrix. The tracing of temperature evolution of their magnetic state unexpectedly evidenced antiferromagnetic (AF) interaction of MNPs with matrix resulting in decreasing the sample magnetization and in formation of unusual domains into the matrix in process of sample magnetic ordering below T_C . The comparison of T -evolution scenarios in the compounds under study indicates higher T_C and larger coercivity at employment of “magnetic” doping by Co that is important for practical applications. At last, we confirm the hypothesis on a spatial magnetic heterogeneity as a reason of irreproducibility of magnetic properties for glassy porous carbon-based nanomaterials using more structurally homogeneous Co-doped sample [18].

2. Experimental details

The porous glassy carbon samples doped with 0.004 mass% of Au (S-Au) and with 0.117 mass% of Co (S-Co), which have been prepared and studied earlier in [17,18], were investigated. Preparation details have been described in Ref. [17]. The atomic force microscopy investigations of the samples doped with Ag, Au and Co provided evidences for the presence of carbon nanoparticles with a broad size distribution given by the average, $R_{av} \sim 60 \text{ nm}$, and the maximum, $R_{max} \sim 110 \text{ nm}$, particle radii in all the above listed samples [17].

To testify a spatial magnetic heterogeneity of glassy porous carbon-based materials we used more homogeneous (according structural data) Co-doped sample [18]. Two small bits: bit 1 with mass $m_1 = 9.6 \text{ mg}$, and bit 2 with $m_2 = 14.5 \text{ mg}$ cutting in a form of a plate from different parts of as-prepared S-Co were used for NLR study. In experiments sample plane was oriented parallel to the magnetic field $H(t)$, to decrease a possible demagnetization effect. A typical in-plane size exceeded the thickness of the plate by more than five times for both bits. Another piece of S-Co was used in magnetization measurements.

Magnetization, $M(B)$, was measured with a SQUID magnetometer in the magnetic field B up to 5 T by increasing and decreasing the field. The dependence of $M(T)$ was measured in a steady magnetic field B between 1 mT and 5 T, after cooling the samples from 300 K down to 3 K without field (zero-field cooled (ZFC) magnetization, M_{ZFC}) or in the applied field (field-cooled (FC) magnetization, M_{FC}). Thermoremanent magnetization (TRM) was investigated after cooling the samples from 300 K to 3 K in a non-zero magnetic field, then heating in field and reducing the field to zero. The magnetization data are presented below after subtraction of diamagnetic contribution.

The measurements of the second harmonic of magnetization of the longitudinal nonlinear response (NLR- M_2) were performed in the parallel dc and ac magnetic fields, $H(t) = H + h \sin \omega t$ (where $h \approx 14.3 \text{ Oe}$ and $f = \omega/2\pi \approx 15.7 \text{ MHz}$) under the condition of $M_2 \propto h^2$. The latter permits us to analyze the results in framework of the perturbation theory. The real and imaginary phase components of M_2 , $\text{Re}M_2$ and $\text{Im}M_2$ respectively, were recorded simultaneously as functions of H at different sample temperatures between 100 and 350 K. The field H was scanned symmetrically with respect to the origin to inspect the magnetic field hysteresis of the signal. It is convenient for control of a spontaneous FM moment arising in a sample since according to symmetrical properties of M_2 only in this case $M_2(H=0) \neq 0$. The amplitude of H -scan was 300 Oe. The

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